and join the still sparsely populated roots of modern clades.

As emphasized by Giles *et al.* and others[16], the early Carboniferous is increasingly being recognized as a key episode in the history of modern vertebrate diversity. Alongside the origin of modern tetrapods, the root of the actinopterygian crown group probably lies somewhere in this interval, as does the first ascent of the ray-finned fishes towards ecological prominence. But polypterids as we now understand them emerge as a Mesozoic phenomenon, with their earlier ancestry perhaps barely distinguishable from that of other early members of the ray-finned clade. Polypterid shape looks increasingly specialized, including those remarkable — and now apparently deceptively primitive — pectoral fins[2,3]. ■

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MATERIALS SCIENCE

Nanomagnets boost thermoelectric output

The direct conversion of heat into electricity — a reversible process known as the thermoelectric effect — can be greatly enhanced in some materials by embedding them with a small number of magnetic nanoparticles.

SEE LETTER P.247

STEPHEN R. BOONA

Thermoelectric materials can convert waste heat into electrical energy, and have applications in both power generation and cooling. The efficiency with which the conversion occurs is quantified in part by the thermoelectric figure of merit *ZT*. On page 247, Zhao *et al.*[1] report a remarkable advance in the search for high-efficiency thermoelectric materials. The authors use a material based on the semiconductor cobalt antimonide ($CoSb_3$) to show that the addition of a small number of cobalt nanoparticles — equivalent to just 0.2% of the material's total mass — substantially increases the material's *ZT*. The technique could potentially improve the efficiency of a wide range of thermoelectric materials.

The quantity *ZT* parameterizes several properties that relate to how heat and electricity flow through materials. Because these properties are intrinsic to the materials, the efficiencies of thermoelectric coolers and generators are independent of their size — unlike, for example, refrigerators driven by vapour compression, or internal combustion engines. In principle, this means that thermoelectric devices offer superior performance over mechanical heat engines in situations requiring less than about 100 watts of power[2].

In practice, however, the inefficiency and impracticality of current thermoelectric technologies largely relegates them to niche applications in which their other advantages over conventional systems — such as reliability, scalability and lack of vibrations — outweigh their inefficiency. For example, they can be used to cool detectors in electron microscopes and to power space probes as they drift between planets[3].

Because thermoelectric coolers represent one of only a few practical tools for cooling matter, an improvement in thermoelectric technology is potentially valuable for both power-generation and temperature-control applications. Accomplishing this goal will require us to identify materials or physical mechanisms that boost *ZT*. Zhao and colleagues take an important step in this direction by showing that the *ZT* of certain materials can be enhanced by exploiting magnetic nanoparticles (nanomagnets). As a demonstration, they consider $CoSb_3$-based materials embedded with cobalt nanoparticles.

NATURE

50 Years Ago

In this paper we describe the synthesis from hydrogen cyanide of yet a further class of compounds—polymers that are readily converted by water to peptide like solids … In the reducing atmosphere of primeval times direct synthesis of polypeptides would have been highly favoured as hydrogen cyanide was certainly a major component of the atmosphere. We suggest that after polymerization and modification in the presence of other reactive molecules such as hydrogen sulphide and acetylene, the prototypes of today's proteins were formed after the macromolecules settled into the cold oceans. As the process of molecular evolution continued, this protein-dominated material gave rise to protein-directed life.
From *Nature* 16 September 1967

100 Years Ago

During the year under review four new entomological field laboratories have been erected in several parts of Canada … In a country like Canada, the administration of the Destructive Insect and Pest Act naturally involves a good deal of routine work. More than 2¼ millions of imported trees and plants were examined in 1914–15. This work had special reference to gipsy moth and brown-tail moths and other foreign insect pests … It appears that the intensity of the infestation of these two moths in Nova Scotia and New Brunswick has decreased, though the area over which they have spread has become extended. An excellent feature is the co-operation which has taken place with the U.S. Government in suppressing these pests, and in introducing into Canada certain of their more important insect enemies.
From *Nature* 13 September 1917

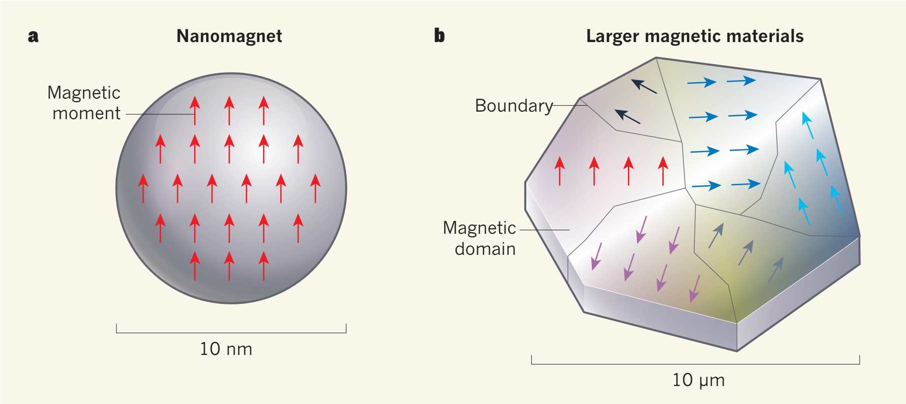

Figure 1 | Two types of magnetic structure. **a**, Magnetic nanoparticles (nanomagnets) are so small that the magnetic moments of their atoms must all point in the same direction — there isn't enough room for multiple magnetic 'domains' to form. As a result, nanomagnets essentially behave like a single magnetic moment. **b**, By contrast, multiple domains form in magnetic materials larger than nanomagnets, producing a mosaic structure in which there are well-defined boundaries between the domains. Zhao *et al.*[1] demonstrate that the single-domain behaviour of sufficiently small nanomagnets can be exploited to enhance the properties of thermoelectric materials, which are used to convert heat into electricity.

The key to the nanomagnets' substantial impact on *ZT* is their diminutive size. The particles are so small that the magnetic moments of their 10,000 or so atoms must all point in the same direction — there isn't enough room for multiple magnetic 'domains' to form (Fig. 1a). Single-domain particles essentially behave like a single super-sized magnetic moment. Zhao and colleagues' particles are so small that they display a phenomenon known as superparamagnetism, in which the super-sized magnetic moment can randomly change direction under the influence of temperature fluctuations.

By contrast, in larger, macroscale volumes of magnetic material — such as in refrigerator magnets — multiple magnetic domains form. Although the magnetic moments of the approximately 10^{23} atoms in a refrigerator magnet point in the same direction as their nearest neighbours, it is energetically favourable for magnetic moments in distant regions to point in other directions (Fig. 1b). This produces a mosaic magnetic-domain structure in which well-defined boundaries separate the different domains. In many respects, such a structure is analogous to (and often correlative with) the microstructure that forms in aggregates of crystalline grains called polycrystals, in which boundaries separate grains of different crystallographic orientation.

The absence of magnetic domains in superparamagnetic nanoparticles imbues them with properties that are different from those of conventional magnets. For example, the nanoparticles' magnetic moments are pinned in one direction by an energy barrier that blocks them from reorienting. As the temperature of the nanoparticles rises, increasingly energetic thermal fluctuations eventually cause the magnetic moments to collectively change direction. Zhao *et al.* determine that, in their materials, this transition occurs at a temperature of about 442 kelvin — comfortably below proposed operating temperatures for CoSb$_3$-based devices[3].

Zhao and colleagues conclude that the embedding of cobalt nanoparticles affects their materials' thermoelectric properties in three main ways. First, each nanoparticle — comprising 10,000 or so metallic atoms — acts as a reservoir for 10,000 or so free electrons, improving electrical conductivity. Second, the fluctuating superparamagnetic moments selectively scatter electrons, enhancing the Seebeck coefficient — a measure of the voltage produced by a material in response to an applied temperature difference. And finally, the presence of randomly distributed nanoscale particles impedes heat flow.

The authors show that these three factors combine to enhance the *ZT* of their materials. In particular, the team finds that when cobalt nanoparticles make up 0.2% of the material's total mass, the *ZT* increases from about 1.3 to nearly 1.8. This value is not the largest ever seen; that distinction goes to multiple reports of *ZT* exceeding 2 in materials based on lead telluride (PbTe)[4,5], tin selenide (SnSe)[6,7] and, earlier this year, copper selenide (Cu$_2$Se)[8]. The main innovation of the current work is the substantial relative increase in *ZT*, in addition to the concept's originality and apparently general applicability — the authors observe a similarly enhanced *ZT* when iron or nickel nanoparticles are used instead of cobalt, and there are probably other, as yet unidentified, material combinations that will also boost *ZT* thanks to this mechanism.

Demonstrating this concept in other materials systems would help to validate Zhao and colleagues' interpretation of how and why nanomagnets improve thermoelectric efficiency. One of the study's weaknesses is that it does not fully explain the physics behind the enhanced Seebeck coefficient. The authors have interpreted the enhancement as arising, at least in part, from changes in electron scattering. If this explanation is correct, their materials could have other scientifically interesting electron-transport properties at cryogenic temperatures[9].

The authors' conclusions also invoke a key assumption that electrons primarily scatter off specific types of vibration in the materials' atomic lattices, as opposed to ionized impurities or other similar features. This assumption could be tested experimentally by carrying out temperature-dependent measurements of the Nernst coefficient — a quantity similar to the Seebeck coefficient, but with the voltage measured perpendicularly to the applied temperature difference and with a magnetic field applied in the third perpendicular direction. The presence of nanomagnets in the authors' materials means that the materials will react differently to an applied magnetic field compared with conventional semiconductors. In particular, their Nernst coefficients will have an extra contribution, which could originate from many different phenomena[10]. Extracting the materials' underlying Nernst coefficients would require the use of magnetic fields that are strong enough to align all of the nanoparticles' magnetic moments.

Nevertheless, transferring this concept from a laboratory demonstration to real-world applications could prove challenging for other reasons. For instance, production of air-sensitive transition-metal nanoparticles, such as those used by Zhao *et al.*, requires delicate synthesis and processing steps, and it is not clear how stable the embedded nanoparticles will be against agglomeration and growth when held for extended times at elevated temperatures. It is also not obvious how easy it will be to find other promising material combinations, because of the need to consider widely varying parameters such as how easily electrons move from the metallic-nanoparticle reservoirs into the surrounding lattice. Addressing these and other challenges will require thoughtful planning and further experimentation, but, in the meantime, the authors' encouraging results illuminate a path along which additional discoveries are likely to be made. ■

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